

# Thermodynamics: The Oldest Branch of Earth Sciences?

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1811-5209/10/0006-0287\$2.50 DOI: 10.2113/gselements.6.5.287

**All geological changes result from the transfer of matter and energy, the study of which is the goal of thermodynamics. Investigating natural processes thus necessarily involves thermodynamic considerations. This has long been practiced implicitly, as shown by the smart reflections made by “natural philosophers” from antiquity to the 18<sup>th</sup> century about topics ranging from atmospheric phenomena to the early history of the Earth. Since the early 19<sup>th</sup> century, investigations explicitly take advantage of a rigorous framework that deals with chemical and thermal aspects of the Earth’s activity. Far from being abstruse, these principles can in fact be summarized in a simple and concise way.**

KEYWORDS: Earth’s history, phase changes, solution models, thermodynamic principles

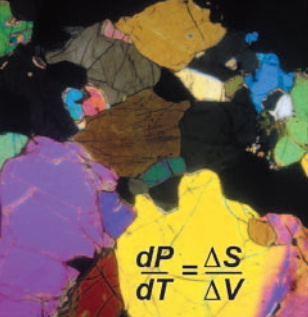
## INTRODUCTION

*Thermodynamics.* The word sounds intimidating. The heat engine, complicated cycles and the entropy conundrum come to mind. And when geological applications are mentioned, people often wonder how useful results can be obtained for an object as complex and as big as the Earth. As a matter of fact, the newly born science called *thermodynamics* rapidly tackled many problems that were far removed from the mutual conversion of heat and work. Its theoretical framework was so flexible that, as shown by J. W. Gibbs (1839–1903), it could also account for any kind of chemical transformation. This should not have come as a surprise. Ever since the very beginning of science in Greece, natural phenomena had been a rich source of reflection. Without knowing it, early “natural philosophers” practiced thermodynamics qualitatively. The fundamental problem of change, which was at the basis of their thought, would in fact fall fully within the precinct of this discipline. Indeed, change results from transfer of matter and energy among the various parts of any system. This issue of *Elements* thus gathers a series of short reviews illustrating how thermodynamic methods are used to derive valuable information about the present and past of our planet, from its atmosphere to its core.

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Olivine (yellow), pyroxenes (brown and violet) and spinel (black) as seen in a thin section of peridotite from Saint Thibéry (Languedoc, France). As embodied in the Clausius-Clapeyron equation, the stability of spinel indicates a source 30 to 60 km deep. PHOTOGRAPH BY NICOLE SANTARELLI

## THERMODYNAMICS WITHOUT A NAME: A HISTORICAL PERSPECTIVE

Key ingredients of thermodynamics were recognized at the very beginning of science through observation of terrestrial phenomena. For instance, what we call today *phase transitions* was at the root of the reflections of Anaximenes (circa 550–480 BC). One of the earliest natural philosophers, he asserted that clouds, rain

and hail were the results of progressive condensation of air, snow forming instead when some air got entrapped in the process. Shortly after, hail was explained in a remarkably accurate way by Anaxagoras (circa 500–428 BC). He stated that water freezes “when a cloud is pushed into the upper region, which is colder because there the reflections of the rays of the sun from the Earth cease.” For this reason, he thought that “hailstorms occur more often in summer and in hot places, because the greater heat pushes the clouds higher up from the Earth.” Anaxagoras also understood that the salinity of seawater resulted, in modern parlance, from water–rock interactions. “Water that is percolated through the earth and washes it becomes brackish,” he asserted, “because the earth has these sorts of flavours in itself.” As a proof, he noted that “both salt and niter [sodium carbonate] are mined from the earth.”

At the same time, fundamental chemical principles were laid down by Empedocles (circa 495–435 BC) in his famous theory of the four elements. As illustrated by a burning log of green wood, which releases smoke, water and ash along with fire, everything was made up of *air*, *water* and *earth*, which represented our gas, liquid and solid states of matter, respectively; *fire*, on the other hand, was posited to be the main agent of change, something akin to our concept of energy. Because elements were indestructible and assembled in specific proportions in everything, conservation of mass and the notion of chemical composition were in addition sketched out. This theory would reign practically undisputed for more than two millennia because of the explanations it provided for a very wide range of phenomena. The Earth was a case in point. By assuming in *On the Heavens* that each element was moving spontaneously to its “natural” place, upward for air and still more so for fire, and downward for water and earth, Aristotle (circa 384–322 BC) accounted in a single stroke for gravity (and what is called today *equipotential surfaces*), the spherical figure of the Earth and the existence of

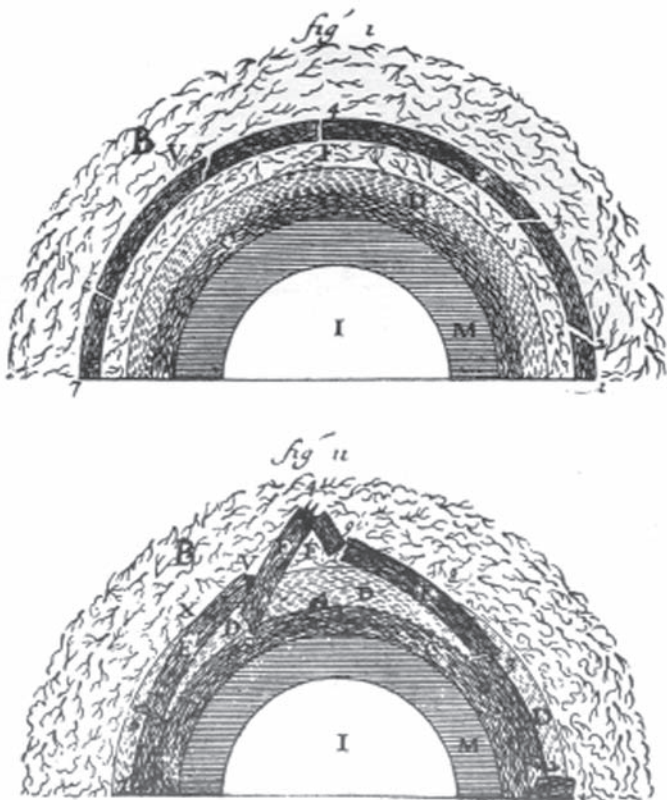
concentric envelopes of atmosphere, hydrosphere and lithosphere. Because the natural place of fire was at high altitude, however, Aristotle's unification of chemistry and geodesy implied that fire could not reside permanently deep in the Earth. Hence, volcanic activity could only be accidental. In yet another implicitly thermodynamic fashion, Aristotle thought that heat was produced by friction of strong winds in subterranean caves, an idea that was subsequently abandoned in favour of combustion of grease, coal, sulfur or bitumen, which were present underground here and there. It then followed that water was the main agent that shaped and reshaped the Earth's surface in a world that was thought to be eternal.

After the advent of Christianity, the world was in contrast firmly believed to have been created a few thousand years ago (see Richet 1999), but water remained the main geological agent. At last fire entered the picture when, in his bold attempt to deduce the whole history of the world from a few first physical principles, René Descartes (1596–1650) claimed that the Earth was a former star that had cooled down and eventually acquired a layered structure with a solid crust overlying a shell of water (Fig. 1). Heated by the Sun, the water caused the crust to crack and form mountain ranges while it gave rise to the seas surrounding the plains. The idea was developed shortly after by another famous philosopher, Gottfried Wilhelm Leibniz (1646–1716). In a book published posthumously (Leibniz 1768), he stated that the Earth was first completely melted and then crystallized to form a thick mass of primitive granite rock, which was ubiquitous on continents, and a hot aqueous solution that yielded the oceans on cooling.

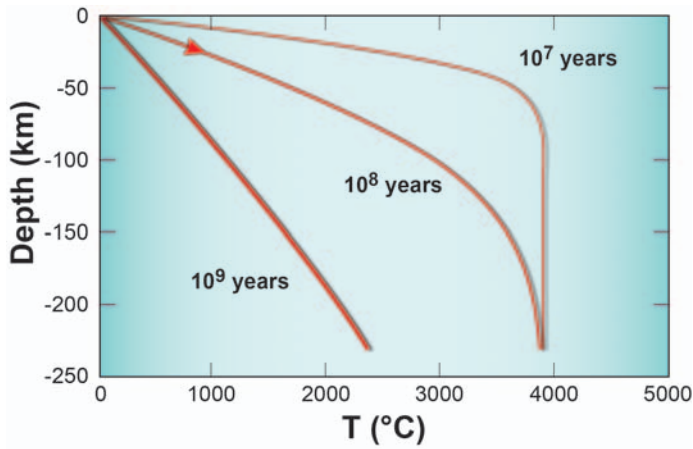
Of course, such ideas are reminiscent of current research themes, but their immediate consequence was to induce a series of breakthroughs. First, Georges-Louis Leclerc, comte de Buffon (1707–1788), took up Leibniz's thesis to establish the immensity of geological time from experiments. He measured the rate of cooling of small balls made up of different substances and then boldly extrapolated his results to an object of the Earth's size. While stating that the Earth was 75,000 years old (Buffon 1779), he wrote in his private notebooks that its actual age of more than 10 million years was in fact much too great to be grasped by the human mind (cf. Richet 1999). To give a firm basis to Buffon's thesis, Joseph Fourier (1768–1830) theoretically investigated heat conduction. By properly distinguishing the capacity of matter to store heat (heat capacity) and transfer it (thermal conductivity), he arrived in 1822 at his celebrated heat equation. This equation and both of these fundamental thermal parameters are thus direct by-products of the age-of-the-Earth problem. In the end, however, Fourier refrained from solving himself his equation for a cooling Earth because of the lack of reliable heat capacity and thermal conductivity data. Nonetheless he did calculate in 1824 that the temperature of outer space was about  $-70^{\circ}\text{C}$ , and not much lower as was incorrectly thought at that time.

Meanwhile, in Scotland, James Hutton (1726–1797), a friend of James Watt, also acknowledged the fundamental role of fire. Hutton considered the Earth as a heat engine in order to introduce the notion of "geological cycle." In a first step, he proposed, underground fire causes orogenesis; in a second, erosion levels out mountains and deposits sediments on the seafloor, after which a new cycle can take place. In fact, heat reaches the Earth's surface from outside (the Sun's heat) and inside (the "primitive" or "central" heat of Leibniz and Buffon). The relative importance of these contributions would remain a matter of controversy until accurate observations were performed. Systematic temperature measurements in mines led Louis Cordier (1777–1861) to define an average geothermal gradient of  $1^{\circ}\text{C}/30\text{m}$  and to conclude, through another bold extrapolation, that the Earth was a ball of fire covered by a thin solid crust about 50 km thick (Cordier 1827) – a view that is still prevalent in the popular mind! The influence of central heat at the Earth's surface was soon found to be negligible, however, when Claude Pouillet (1780–1868) measured the heat flux from the Sun as  $1.76\text{ cal}/(\text{min} \cdot \text{cm}^2)$  (Pouillet 1838). But the real significance of the result was that the Sun was emitting so much heat that a 17 km thick layer of ice present at its surface would be melted in a day. In other words, it would take less than 5000 years for the star to burn up entirely if it were composed of the best quality coal. The fundamental problem of the age of the Sun and solar system was thus raised by a simple calorimetric argument.

The stage was set for William Thomson (1824–1907), who was to become baron Kelvin of Largs, to enter the fray. A pioneer of "thermo-dynamics," he kept throughout his life a keen interest in geology that began in his youth (Thomson 1894). Solving Fourier's equation for an Earth assumed to be initially molten at a temperature of  $3870^{\circ}\text{C}$ , he found that between 20 and 400 million years were required to yield the geothermal gradient measured by Cordier (Fig. 2). Following Hermann von Helmholtz (1821–1894), he then assumed that the energy radiated by the Sun resulted from gravitational contraction, a process that could not last for more than 100 million years. Using two completely independent methods, Kelvin thus derived similar ages for both the Earth and the Sun. This most impressive achievement split the geological community and gave rise to a celebrated



**FIGURE 1** The Earth's internal layered structure as first depicted by Descartes (1644) before (TOP) and after (BOTTOM) mountain formation caused by the phase change of the subterranean water. I: primal, originally "subtle" stary matter; M: opaque body, similar to the "crust" of sunspots; D: water; B and F: air



**FIGURE 2** Age of the Earth as determined by Kelvin from a comparison between the geothermal gradient measured by Cordier near the surface (arrow) and the temperature profiles he calculated from the Fourier heat equation for three ages of the Earth and a uniform initial temperature of 3870 °C. In his later years, Kelvin narrowed down his estimate of the age of the Earth to 24 million years.

geological controversy (Burchfield 1990). Because Kelvin assumed that there was no heat production within the Earth, the discovery of radioactivity eventually ruined his conclusions and incidentally opened the way to solving the star energy problem (Richet 1999). Nonetheless, Kelvin's legacy is still alive through the strong emphasis he put on quantitative measurements and modelling of Earth processes, which some might take erroneously as quite recent ideas.

## THERMODYNAMICS IN A NUTSHELL

In the very first application of chemical thermodynamics to geology, Jacobus H. van't Hoff (1852–1911) accounted for crystallization of salts from brines. After the Earth had for so long been a source of inspiration for thermodynamics, geology was beginning to benefit from concepts set forth by physicists and chemists. As signaled by Fourier, the turning point had been the change from qualitative to quantitative methods, which led to the two fundamental laws of thermodynamics, namely, the conservation of energy and the increase of entropy for spontaneous transformations in a closed system. At a conceptual level, the major advance had been the introduction of entropy to account for the fact that one kind of energy, heat, is “a little more equal” than the others.

Notwithstanding this peculiarity of heat, all forms of energy are expressed in the same way and their changes take place in the same manner (see Richet 2001 for a detailed account). For instance, electrical energy ( $E_{el}$ ) is the product of potential ( $U_e$ ) and charge ( $q$ ).  $U_e$  is an *intensive* property, remaining constant if, others things being equal, the size of the system of interest is, for example, doubled; on the other hand,  $q$  is an *extensive* property and is proportional to the size of the system. Electrical charges are neither created nor destroyed: they are *conservative*. And we know that electrical energy changes only through transfer of charge between different potentials, not through transfer of potential between different charges, so that

$$E_{el} = U_e q \quad \text{and} \quad dE_{el} = U_e dq . \quad (1)$$

The transformation is spontaneous when charges are transferred from a high to a low potential. During transfer, the high potential from which the charges move decreases, the low potential toward which the charges go increases, and

the transfer ceases when both potentials have become equal. A state of *equilibrium* is thus reached when a transfer of *extensity* (electrical charge) has ensured an equal *tension* (potential) in the two reservoirs of energy involved.

In geological thermodynamics, the relevant kinds of energy are mechanical, chemical and thermal. For all of them, the formalism just described for electrical energy applies. For mechanical energy ( $W$ ), the tension is of course pressure. If a system is split into two subsystems with different pressures and the boundary between them is allowed to move spontaneously, the volume of the high-pressure part will increase at the expense of that of the low-pressure subsystem until a constant pressure obtains. Because volume is gained by the high-pressure instead of the low-pressure part, however, the extensity of mechanical energy is not volume ( $V$ ), but its negative ( $-V$ ); thus we have

$$W = -PV \quad \text{and} \quad dW = -P dV . \quad (2)$$

For chemical energy ( $G$ ), the extensities are the number of moles of all components ( $n_i$ ) of the system. The tensions are less intuitive. They are called chemical potentials ( $\mu_i$ ) and are defined such that simple expressions analogous to Equations (1) and (2) are obtained, namely,

$$G = \sum \mu_i n_i \quad \text{and} \quad dG = \sum \mu_i dn_i . \quad (3)$$

For thermal energy ( $Q$ ), the tension is again evident: it is temperature ( $T$ ). The extensity is less obvious; it is entropy ( $S$ ):

$$Q = TS \quad \text{and} \quad dQ = T dS . \quad (4)$$

Contrary to other extensities, however, entropy is not conservative. This is the essence of the second law of thermodynamics, which is not only beyond the scope of this introduction but also largely irrelevant for our present purpose.

We now define the internal energy ( $U$ ) as the sum of these three forms of energy:

$$U = \sum \mu_i n_i - PV + TS . \quad (5)$$

All parameters of Equation (5) are state variables, that is, they do not depend on the history of the system but are unambiguously defined by its current state if *internal equilibrium* prevails. In this case, which is implicitly assumed to hold true in any application of thermodynamics, an important postulate is that only two variables are needed to specify the state of a system once the chemical composition is fixed; for convenience, pressure and temperature are usually selected in geological applications. Equilibrium is reached when tensions become uniform throughout the system, that is, when, entropy has flowed in appropriate amounts from hotter to colder phases, volume has been gained by compressed phases at the expense of less compressed phases and the various components have been transferred from the phases in which their chemical potential was high to those in which their potential was low. For equilibrium between phases  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc., we thus have simply

$$T^\alpha = T^\beta = T^\gamma = \dots = T , \quad (6a)$$

$$P^\alpha = P^\beta = P^\gamma = \dots = P , \quad (6b)$$

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots . \quad (6c)$$

Prediction of phase equilibrium at constant  $T$  and  $P$  then boils down to solving Equation (6c) for the system of interest. As an illustration, consider equilibrium between water and water vapour, or any two pure phases, in which case  $n_i = 1$  and  $\mu_i = G_i$ . We first define enthalpy as  $H = U + PV$ , and rewrite Equation (5) in another way:

$$G = \sum \mu_i n_i = U + PV - TS = H - TS , \quad (7)$$

before renaming  $G$  as *Gibbs free energy*. It follows that the experimentally measurable isobaric heat capacity ( $C_p$ ) at constant pressure,

$$C_p = (\partial H/\partial T)_P = T (\partial S/\partial T)_P, \quad (8)$$

allows the temperature dependence of  $G$  to be determined for a given phase. Its pressure dependence is given by

$$(\partial G/\partial P)_T = V, \quad (9)$$

and it can also be determined readily if the *equations of state*, namely, the relations between  $P$ ,  $T$  and  $V$ , are known for the phases of interest. Solving Equation (6c) to find the  $P$ - $T$  curve at which the two phases coexist is thus tantamount to solving the equation

$$\Delta\mu_i = \Delta G = [\Delta H(T_0) + \int_{T_0}^T \Delta C_p dT] - T[\Delta S(T_0) + \int_{T_0}^T \Delta C_p/T dT] + \int_{P_0}^P \Delta V dP = 0 \quad (10)$$

This can be done numerically if  $\Delta C_p$ ,  $\Delta H(T_0)$  and  $\Delta S(T_0)$  are known from calorimetric experiments and if the equations of state of the two phases are also known.

The criterion (6c) is readily used when only one or two components have to be considered. For more complex systems, it can be expressed in more convenient ways. For instance, an equivalent criterion is that the Gibbs free energy be minimum for a system in equilibrium at constant  $P$  and  $T$ . Strictly speaking, however, systems with pure phases do not exist because all components have to be present in all phases, possibly at vanishingly low concentrations, otherwise Equation (6c) would not be satisfied. A low concentration actually results from a basic structural incompatibility between a given component  $i$  and its host phase  $\alpha$ , causing  $\mu_i^\alpha$  to increase strongly with increasing amounts of  $i$ . High concentrations are, in contrast, found when there is an excellent structural match, so that  $\mu_i^\alpha$  increases slowly. Hence, the fundamental problem in chemical thermodynamics is to know how chemical potentials vary with composition. In the ideal solution model, one

assumes that components mix at random without thermal effects, in which case one finds that, at constant  $T$  and  $P$ , chemical potentials are simple functions of mol fractions ( $x$ ):

$$\mu_i = \mu_i^\circ + RT \ln x_i, \quad (11)$$

where  $R$  is the gas constant and  $\mu_i^\circ$  is the chemical potential of component  $i$  in its standard state (that is, at the  $T$  and  $P$  and in the structural form for which thermochemical data are most conveniently determined).

The ideal model is a good approximation for gases at low pressure, for which molecular interactions are weak, but generally not for aqueous solutions, silicate melts or solid solutions. For real solutions, however, the analytical form of Equation (11) is so convenient to treat chemical equilibria that the activities ( $a$ ) of the components are defined such that chemical potentials are, by definition, given by

$$\mu_i = \mu_i^\circ + RT \ln a_i. \quad (12)$$

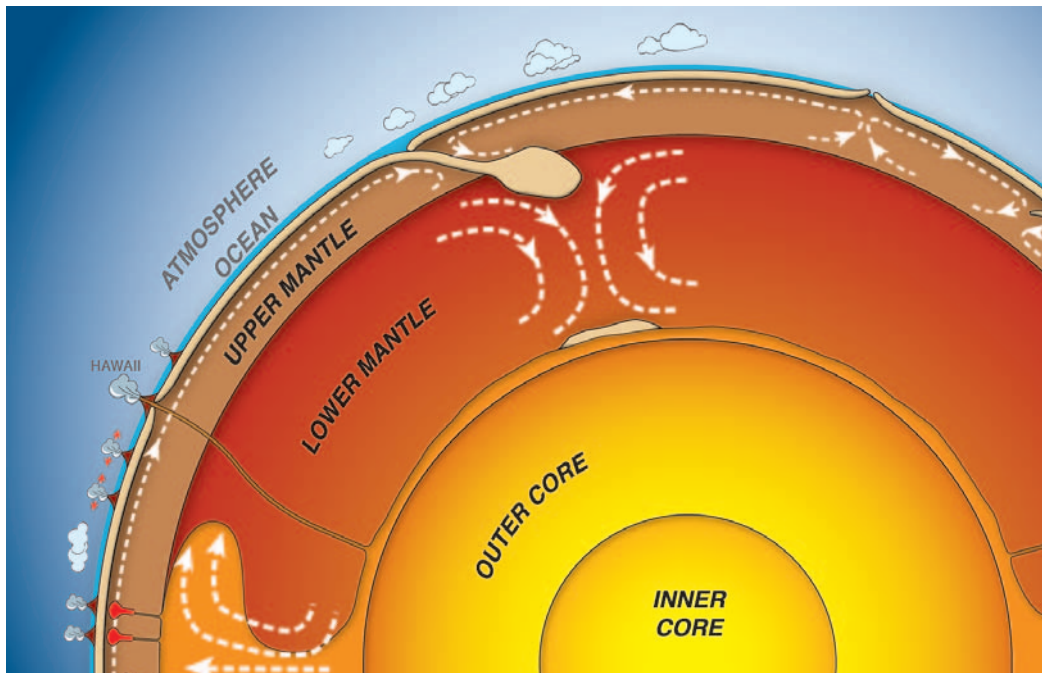
And because mol fractions are the compositional parameters that can be measured, it is useful to relate them to activities via activity coefficients ( $\gamma$ ),

$$a_i = \gamma_i x_i, \quad (13)$$

so that  $\gamma_i = 1$  and  $a_i = x_i$  in an ideal solution. In summary, Equations (10) and (12) represent the needed formalism to calculate chemical equilibrium once the relations in Equation (13) are known. It is beyond the scope of this review to show how these relations are determined. Suffice it to say that the most reliable results are obtained when calorimetric and phase equilibria data are appropriately combined. Examples will be found in the following articles of the use of the principles briefly summarized here for equilibrium thermodynamics calculations.

## IN THIS ISSUE

As was envisioned by Descartes, the Earth is made up of several concentric shells, the atmosphere, hydrosphere, crust, mantle and core (FIG. 3). The very existence of these envelopes indicates that they are separated by rather sharp



**FIGURE 3** The Earth envelopes as currently depicted, with subducting slabs, convection cells and ascending plumes.

boundaries through which exchange of matter and energy is more or less limited. In the atmosphere and hydrosphere, energy comes primarily from the Sun. In the solid Earth, in contrast, energy has a deep origin and represents a combination of gravitational energy transformed into heat during the original accretion of the planet, radioactive energy and the heat released by very slow crystallization of the outer core. In all shells, however, the input of energy is dissipated either physically through mass transfer or chemically through a great many kinds of reactions.

From the atmosphere to the deepest recesses of the Earth, the examples in this issue of *Elements* illustrate the diversity of approaches offered by thermodynamics to solve specific questions. First, Bott (2010) discusses how the phase changes of water in the atmosphere account for various meteorological observations. Then, Millero and DiTrollo (2010) describe the effects of CO<sub>2</sub> dissolution on chemical equilibrium in the ocean, an important topic with respect to the current climate debate. How rocks and aqueous solutions interact is described in Zuddas (2010). Powell and Holland (2010) relate how the investigation of metamorphic reactions, which involve complex solid solutions, serves to decipher the history of continents. Continuing the descent, Richet and Ottonello (2010) present phase equilibria involving magmas, the agents that have most efficiently transferred heat and matter throughout geological history. In the final article, Saxena (2010) considers important aspects of the structure and dynamics of the mantle and core.

To some it might seem surprising that kinetic factors and irreversible effects can be so consistently ignored. For acid-base reactions in water the kinetics are indeed extremely rapid, but they are very slow for mineral reactions. Nonetheless, thermodynamics can be applied successfully

in both cases if we follow the key initial step of defining the *system* of interest, that is, that part of the universe whose transformations will be considered at an appropriate timescale. Any observed departure from the equilibrium state can then be used to determine some detail of the process investigated. Perhaps even more important is the fact that the system of interest is defined such that the entropy created through the irreversible nature of actual transformations does not concern it, but only its surroundings. This is the reason why this created entropy can be simply ignored and why the same theoretical framework can be put to use in widely different problems or contexts. At a large scale, adiabatic processes are, for instance, as important in the atmosphere as in the mantle. At a small scale, nucleation and growth in water and silicate melts obey the same rules. These are good examples of the universal applicability of thermodynamics. Albert Einstein (1879–1955) stressed it, when he noted that “a theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability.” Therefore, he remarked on “the deep impression which classical thermodynamics made upon me. It is the only theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.”

## ACKNOWLEDGMENTS

We thank all the authors who have contributed to this issue, as well as Pierrette Tremblay and Hap McSween for all their efforts in getting this issue to production. We also thank Joel Dyon of IGP for drafting the figures of several papers. GSH acknowledges funding from NSERC via a Discovery grant. ■

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## GLOSSARY

**Activity** ( $a$ ) – a state variable characterizing the “effective concentration” of a component in a solution

**Activity coefficient** ( $\gamma$ ) – the ratio between the “effective” and actual concentrations of a component in a solution

**Adiabatic transformation** – transformation at constant entropy

**Chemical potential of a component** ( $\mu$ ) – an intensive state variable characterizing the “strength” of the given component in the solution of interest, which must be the same in all phases of a system to achieve chemical equilibrium

**Component** – any entity that can be used to describe the chemical composition of a system (e.g. Si, O, Si<sup>4+</sup> and O<sup>2-</sup> for silica). The components are *independent* when their number is minimum (2 for SiO<sub>2</sub>; for instance Si and O, or Si<sup>4+</sup> and O<sup>2-</sup>).

**Enthalpy** ( $H$ ) – a state variable accounting for heat exchanged at constant pressure

**Entropy** ( $S$ ) – a state variable accounting for the microscopic distribution of matter and energy throughout a system

**Equation of state** (EOS) – the relationship between the pressure, temperature and volume of a system. The simplest EOS is that of one mol of ideal gases, namely,  $PV = RT$ , as it does not depend on any parameter specific to the substance considered. For solids, liquids or dense gases, more complex equations must be used. Along the geothermal gradient, the thermal expansion due to increasing temperature is small compared to the compression resulting from high pressure. Only the latter effect will thus be described here through the Birch-Murnaghan equation used extensively in geophysics. At constant temperature, this EOS relates pressure and volume to the bulk modulus,  $K_T$ , and its first pressure derivative,  $K'_T$ , by

$$P = 3/2 K_{T0} [(V_0/V)^{2/3} - (V_0/V)^{5/3}] [1 + 3/4 (K'_{T0} - 4)[(V_0/V)^{2/3} - 1]] \quad (14)$$

$$K_T = K_{T0} (V_0/V)^{5/3} [1 + (3/2 K'_{T0} - 5/2) [(V_0/V)^{2/3} - 1]] \quad (15)$$

$$K'_T = (\partial K/\partial P)_T = K'_{T0} \quad (16)$$

where the subscripts 0 indicate the value of  $V$ ,  $K_T$  and  $K'_T$  at zero pressure. These equations are actually derived from a 3<sup>rd</sup>-order expansion of the Helmholtz free energy in terms of finite strain. Empirically, their validity is justified by the fact that they account for compression curves as different as those shown in FIGURE 4, with values of  $K_{T0}$  ranging from 3.6 to 4360 kbars for H<sub>2</sub> and diamond, respectively. Its validity is also justified by the fact that values of  $K'_{T0}$  are found to be generally close to 4 (for instance, 4.7 for H<sub>2</sub> and 3.3 for diamond), the value for which Equation (14) reduces to its first term, indicating that the convergence of the expansion is actually rapid.

**Extensive property** – other things being equal, a property proportional to the size of the system (e.g. volume, enthalpy, entropy, Gibbs free energy, etc.)

**First law of thermodynamics** – expresses the fact that energy is conserved in all transformations, i.e. that any variation in a given form of energy is exactly compensated by the variations of others

**Gibbs free energy** ( $G$ ) – the thermodynamic potential for transformations at constant temperature and pressure, which must be minimum for equilibrium to be achieved under these conditions

**Heat capacity** – the temperature derivative of enthalpy at constant pressure ( $C_p$ ) or of internal energy at constant volume ( $C_v$ )

**Intensive property** – a property independent of the size of the system (e.g. pressure, temperature, chemical potential, index of refraction, viscosity, etc.)

**Internal energy** ( $U$ ) – the sum of the kinetic and potential energies over all the degrees of freedom of the particles that constitute a system

**Phase** – a structurally homogeneous portion of matter in a system characterized by the same intensive properties (e.g. all the ice flakes in an ice bath constitute a single phase)

**Phase rule** – a rule stating that the variance,  $v$ , of a system (namely, the number of variables that can be varied without causing a change in the number and nature of the phases that coexist) is given by  $v = c + 2 - \phi$ , where  $c$  is the number of independent components and  $\phi$  the number of phases of the system

**Second law of thermodynamics** – states that the entropy of an isolated system can only increase as a result of spontaneous transformations

**Solution** – a gaseous, liquid or solid phase made up of several components mixed at the atomic scale

• **Athermal solution** – a solution whose components mix without heat effects

• **Ideal solution** – a solution whose components mix randomly and without heat effects

• **Regular solution** – a solution whose components mix randomly but with heat effects. For a binary system, the enthalpy of mixing is given by  $\Delta H_m = W_{12} x_1 x_2$ , where the  $W_{12}$  binary interaction parameter may be considered as temperature dependent and is determined from fits made to the input thermodynamic data. The activity coefficient of the components are then of the form  $RT \ln \gamma_1 = W_{12} (1-x_1)^2 = W_{12} x_2^2$ . As will be seen in the papers in this issue, more complex equations are written for multicomponent systems, but they rest on the same basic assumption of binary enthalpic interactions, i.e.  $\Delta H_m = \sum W_{ij} x_i x_j$ .

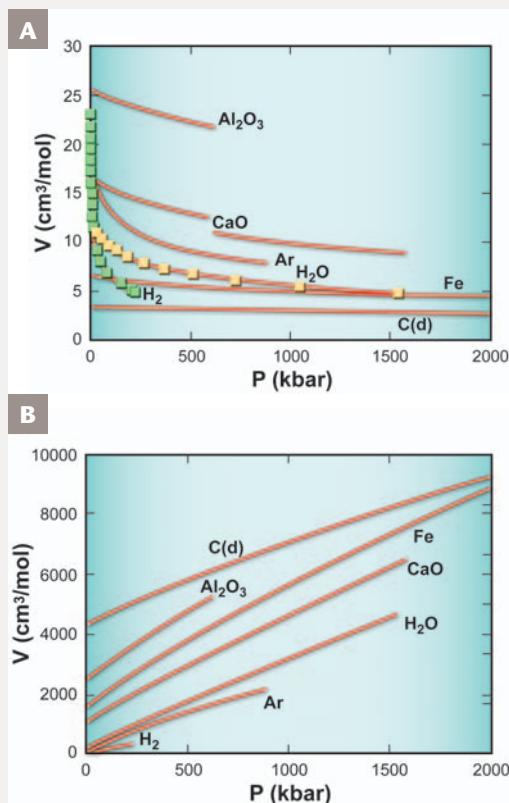
**Standard state of a component** – the reference state chosen for the component of interest, from which changes in thermodynamic functions are evaluated. It is often taken as the pure component in its stable phase at the pressure and temperature considered.

**State** – characterized by the intensive and extensive properties of the constitutive phases of a system

**State variable** – any variable that depends only on the current state of the system and not on its history

**System** – that particular portion of the universe under consideration. A system is open when it exchanges energy and matter with the surroundings and closed if it exchanges only matter.

**Transformation** – any process changing at least one state variable of a system



**FIGURE 4** Room-temperature volume (A) and bulk modulus (B) as a function of pressure. The contrast between the extremely large compression of H<sub>2</sub> and the slight volume change of diamond, C (d), illustrates the very strong dependence of volume properties on the strength of interatomic bonds. DATA FROM RICHTER (2001)